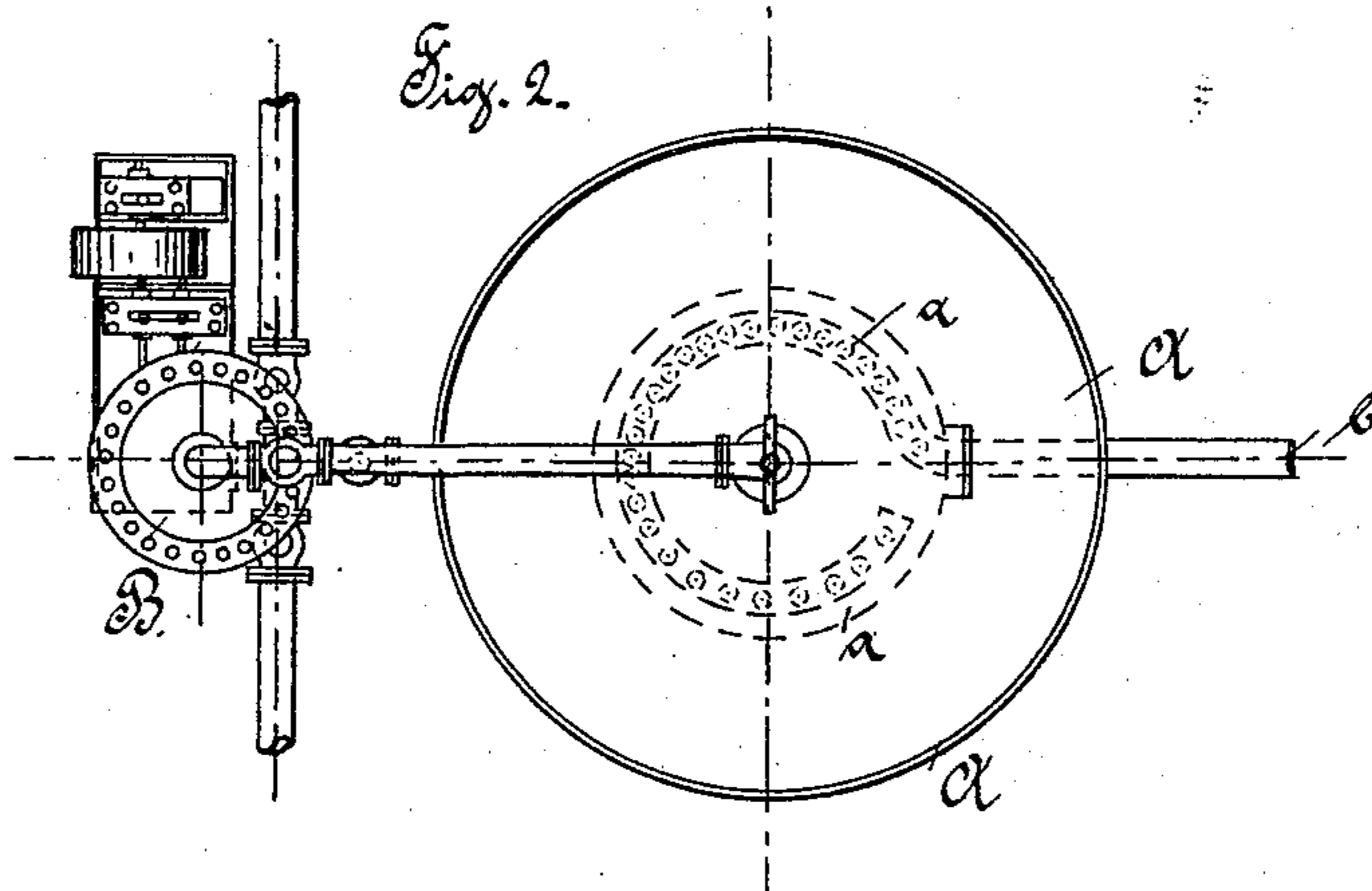
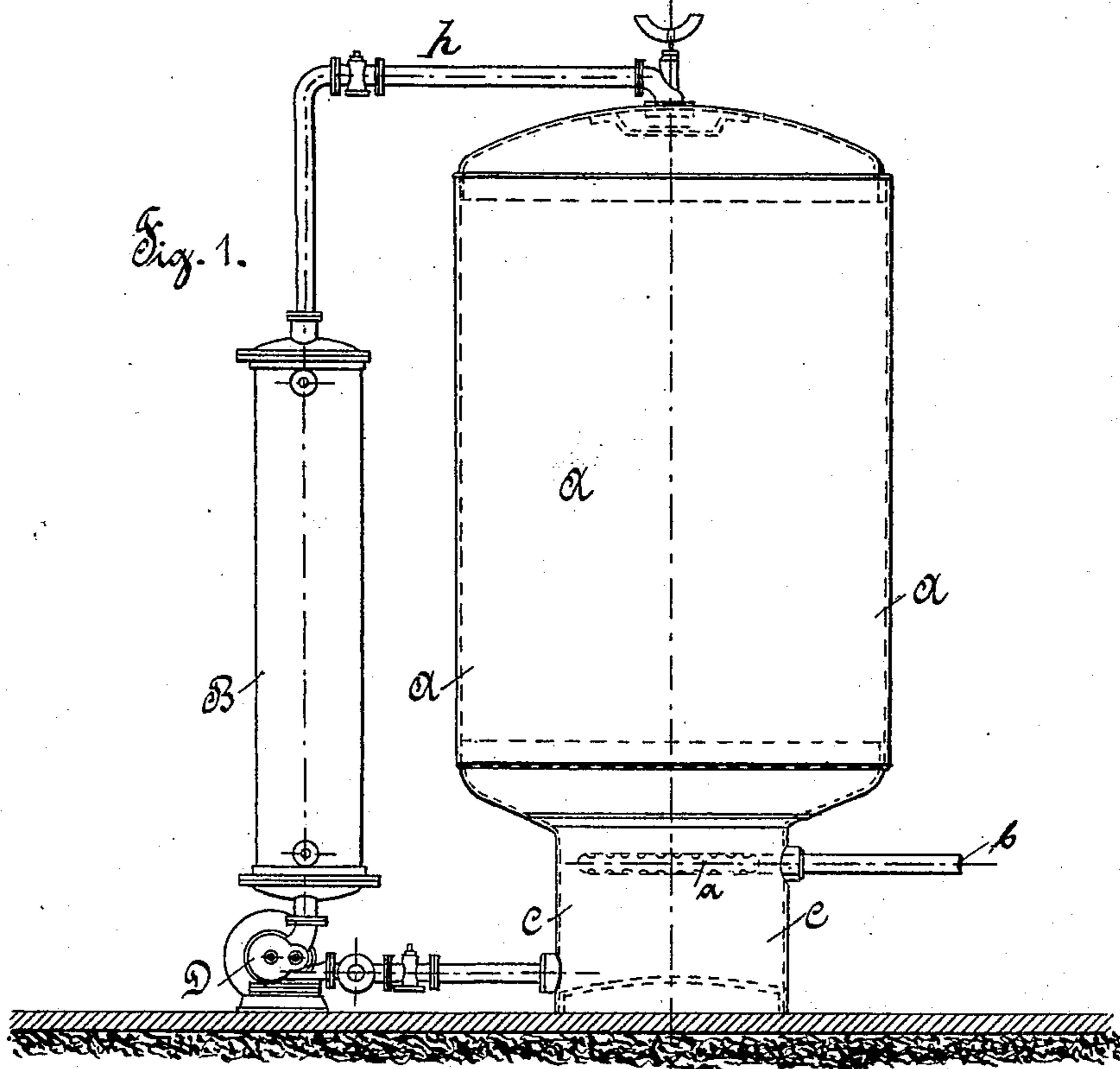


(No Model.)

H. THIES & E. HERZIG.
PROCESS OF BLEACHING.

No. 496,072.

Patented Apr. 25, 1893.



Witnesses:
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UNITED STATES PATENT OFFICE.

HEINRICH THIES, OF LAAKEN, AND EMIL HERZIG, OF REUTLINGEN,
GERMANY.

PROCESS OF BLEACHING.

SPECIFICATION forming part of Letters Patent No. 496,072, dated April 25, 1893.

Application filed November 1, 1890. Serial No. 370,034. (No specimens.) Patented in Germany May 20, 1890, No. 59,674, and July 18, 1890, No. 56,705; in France August 16, 1890, No. 207,671; in England August 18, 1890, No. 12,950, and in Austria-Hungary April 17, 1891, No. 44,564 and No. 76,284.

To all whom it may concern:

Be it known that we, HEINRICH THIES, a subject of the King of Prussia, German Emperor, residing at Laaken, near Barmen Rittershausen, in the Kingdom of Prussia, Empire of Germany, and EMIL HERZIG, a subject of the King of Württemberg, residing at Mulhouse, Alsace, (formerly of Reutlingen,) in the German Empire, have invented certain new and useful Improvements in Bleaching, (for which we have obtained patents in Germany, No. 59,674, dated May 20, 1890, and No. 56,705, dated July 18, 1890; in Austria-Hungary, No. 44,564 and No. 76,284, dated April 17, 1891; in Great Britain, No. 12,950, dated August 18, 1890, and in France, No. 207,671, dated August 16, 1890,) of which the following is a full, clear, and exact specification.

The object of our invention is: first, to subject the fibrous material to a particular preliminary treatment in order to enable the same to stand the action of boiling concentrated caustic lye; second, to prevent destruction of the fiber by the caustic lye by previously neutralizing the action of the oxygen contained in the material; third, to keep the caustic lye at a constant degree of concentration and thereby to reduce the quantity of the said lye used heretofore in the bleaching process and to shorten the latter. We effect by these improvements great economy in time, working-power, steam and chemicals, and cause the waste-waters to be of smaller quantity and better quality than hitherto.

We will now proceed to describe the manipulation of our improved process as applied to calico, referring for a part of the process to the accompanying drawings, in which similar letters denote similar parts throughout the different figures, and of which:

Figure 1 is a side-elevation; Fig. 2 a top view of the apparatus used for the improved process.

The apparatus consists first of the bucking vessel A, which may be closed by means of the cover A'. Below the bucking vessel A, we provide a receptacle C of smaller diameter, and separated therefrom by a horizontal sieve-

plate C'. At a short distance below the latter, there is located a circular horizontal perforated pipe *a*, which connects directly with a straight pipe *b*—not perforated—leading to the atmosphere, as shown, or to a condenser.

E is a pipe connecting the lower part of receptacle C with the chamber of a pump D, which latter is also in communication with a tubular boiler B, by means of the pipe F. The top of boiler B is connected to the top of the bucking vessel A by a pipe *h*. Suitable cocks H H' are provided in pipes E and *h*.

I I' is a pipe for sucking the liquid in at the beginning of the operation and letting it off at the end of the same, and H² H³ are cocks to open and close the passage of either of these pipes.

Our improved process is performed as follows: The dry cotton-cloth or calico is impregnated with a quantity equal to its own weight of an acid solution, each liter of which contains: first, 0.5 gram of hydrofluoric acid of seventy-five per cent, and second, ten grams of sulphuric acid of sixty per cent. water-free acid, or sixteen grams of muriatic acid of thirty per cent. hydrochloric acid gas. The cloth is allowed to lie in this solution for about four hours and then steamed for half a minute. Thereafter the pieces are passed through a washing machine of usual kind. Subsequently the cloth is immersed in an alkaline bath consisting of a solution of about one-half per cent. of soda in water. We allow this bath, the temperature of which is kept at 50° centigrade, to act for up to twelve hours. When the textiles are very impure, for instance through size, or when large quantities of pectine-like bodies adhere to the raw material, the latter manipulation is wholly or partially repeated. Thereafter the calico is washed in a bath containing fifty grams of chloride of magnesium or of another alkaline earth compound in one thousand liters of water. The addition of the first ingredient may be diminished or entirely dispensed with when the wash-water already possesses a high degree of hardness through alkaline earths. The excess of wash-water is pressed off and then the material is

brought with about its own weight of wash-water into the bucking vessel A, and placed on the sieve-plate C' after removing the cover A'.

After the bucking vessel A is closed, the fibrous materials are steamed by the tube system contained in the tubular boiler B; the steam is introduced into the bucking vessel A by means of the tube *h*. The steaming of the materials, whereby the same are brought to a temperature of above 100° centigrade, lasts up to two and one-half hours, according to the size of the boiler. The steam having passed the cloth fills the receptacle C and enters the pipe *a* through its perforations, so that it may continually escape into the atmosphere or the condenser through the pipe *b*; the water formed by partial condensation of the steam is gathered at the bottom of the receptacle C. Now boiling caustic alkaline lye is brought into the vessel A. This lye is prepared in the following manner: Fifty kilograms of soda-salt containing ninety-eight to ninety-nine per cent. of carbonate of soda are dissolved in six hundred liters of water, and we add continually small quantities of slaked lime until all carbonic acid has combined with the lime; then we allow the carbonate of lime to subside and decant the clear liquid. The hereinbefore mentioned quantity of lye is sufficient for fifteen hundred kilograms of calico. In the said clear solution we saponify, prior to using it, about ten kilograms of resin; subsequently the solution is heated to boiling heat and pumped through the boiler B and pipe *h* into the bucking vessel A by means of the pump D. The liquid passing through the fibrous material and accumulating at the bottom of the receptacle C is constantly drawn out of the same by means of the pump D, and forced through the tubular boiler B, the temperature of which is kept about 40° centigrade above that of the bucking lye, and through the pipe *h* back into the bucking vessel A. Thus the liquid constantly circulates through A C E D F B *h*, at a temperature up to 125° centigrade. During this circulation the caustic lye, continually kept boiling, gradually saponifies the greasy impurities of the materials, neutralizing thereby the alkalies of the bucking lye. The weaker action of the latter which results thereof is corrected by the concentration of the same effected by the continuous escape of steam through the pipes *a* *b* below the fibrous materials. This circulation and heating last for about five hours. Subsequently the calico is washed in the bucking vessel A with boiling water and then the usual chloric treatment or chemicking takes place; but we use only one third of the quantity of chloride of calcium that was hitherto required. Finally the cloth is treated in the same way as in the beginning of the process, that is to say impregnated with a quantity equal to its own weight of an acid solution, each liter of which contains: first, 0.5 grams of hydrofluoric acid of seventy-five per cent.,

and, second, ten grams of sulphuric acid of sixty per cent. water-free acid, or sixteen grams of muriatic acid of thirty per cent. hydrochloric acid gas.

We will now proceed to explain the object of each of the steps of the process, and also state under which circumstances some of these steps may be dispensed with. The addition of hydrofluoric acid to the solution of sulphuric or muriatic acid employed for the treatment of the fibers in the beginning of the process, is of great importance, notwithstanding the slight proportions in which this hydrofluoric acid is used. It has been ascertained that, when subjected to this preparatory treatment with the stated addition of hydrofluoric acid, the silica compounds and other organic and inorganic bodies and impurities adhering to the fiber, are considerably more readily dissolved in the further course of the process than when the addition of hydrofluoric acid is not made.

The object and result of the first steaming, which are effected by means of the usual machines, are to prevent basic compounds from being re-deposited on the fibrous materials from acidulous solutions of inorganic salts in the ulterior treatment of the cloth.

In the case of fibrous materials which contain but traces of inorganic compounds, the preparatory treatment with acid may be dispensed with and these materials receive directly the treatment with alkali. The purpose of the latter is to soak or remove, prior to the bucking operation, loosely adhering particles, as for instance size, pectine bodies and dried-in vegetable juices.

The result of the addition of an alkaline earth compound to the wash water is the easy and complete removal of the alkali adhering to the fiber, which alkali was very difficult to remove hitherto, and the formation of a precipitate of an alkaline earth compound on the fiber.

The process is illustrated by the chemical formula: $2\text{NaOH} + \text{MgCl}_2 + \text{H}_2\text{O} = 2\text{NaCl} + \text{Mg}[\text{OH}]_2 + \text{H}_2\text{O}$. This precipitate owing to its slight solubility in water, remains on the fiber notwithstanding the subsequent steaming, and in consequence of its energetic reducing qualities completely absorbs, at the beginning of boiling heat, any amount of oxygen that may have remained in the fiber. The alkaline earth compound deposited on the latter is moreover capable of converting indigo blue and azo colors into the well-known colorless compounds. A further object of the preparation with alkaline earths is completely to neutralize the noxious influence of the caustic alkalies, applied hereafter, on the fiber. When treating the latter with caustic alkalies, directly without the said preparation, it is twisted into a spiral form, whereby the fabric assumes an inferior appearance.

The steaming of the materials immediately preceding the bucking process is intended to expel all air adhering to the fibers, as the

oxygen of said air, when coming in contact with the boiling caustic lye, would cause a destruction of the fibers. We are aware that steaming of the material has been described, 5 but only with the object of moistening the material, and not of expelling the air from the same. Therefore, in the methods known hitherto, the air was allowed to come in contact with the material after the same was steamed, 10 whereas this is most carefully avoided in our improved process.

We do not confine ourselves to the described method of steaming in order to prevent the oxygen from accomplishing its destructive 15 effect, and we may also draw the air out of the fibers in any other manner, as by means of an air pump, or a reducing agent may be used by which the oxygen is chemically bound and thus neutralized. The main feature of 20 this step, immediately preceding the bucking, is that the oxygen of the air still adhering to the fiber should be prevented in some way from exerting any action on the same during the bucking process.

25 The employment of boiling caustic lye is of great importance, as it avoids the shrinking of the fibers known to occur when the same is used cold.

We are well aware that some parts of the 30 process hereinbefore described are known and have been in use in the industry, and therefore we do not claim these parts as our invention. We are also aware that in some bleaching processes a deposit of an alkaline earth 35 compound was formed on the fiber, when steeping the same in a lye of caustic lime; but whereas in that case the formation of said deposit is quite incidental, it is of primary importance in our improved process, and does 40 not take place during the bucking process, but before the same; therefore,

What we believe to be novel in our process, and desire to secure by Letters Patent of the United States, is--

45 1. The process of bleaching consisting in washing the material in a bath containing an alkaline earth compound, and in removing the air adhering to said material, and in treating the same thereafter with boiling caustic 50 alkaline lye, which is kept concentrated by a constant discharge of steam, for the purpose as described.

2. In the process of bleaching washing the 55 material in a bath containing an alkaline earth compound, then steaming said material,

and treating the same thereafter with boiling caustic alkaline lye, which is kept concentrated by a constant discharge of steam, for the purpose as described.

3. The process of bleaching consisting in 60 first immersing the material in a solution containing hydrofluoric acid, and in washing said material in a bath containing an alkaline earth compound, and in removing the air adhering to 65 said material, and in treating the same thereafter with boiling caustic alkaline lye, which is kept concentrated by a constant discharge of steam, for the purpose as described.

4. The process of bleaching consisting in 70 immersing at first the material in a solution containing hydrofluoric acid, and in washing said material in a bath containing an alkaline earth compound, and in steaming said material, and in treating the same thereafter with 75 boiling caustic alkaline lye, which is kept concentrated by a constant discharge of steam, for the purpose as described.

5. The process of bleaching consisting in immersing at first the material in a solution 80 containing hydrofluoric acid, and in steaming the same, and in washing said material in a bath containing an alkaline earth compound, and in removing the air adhering to said material, and in treating the same thereafter 85 with boiling caustic alkaline lye, which is kept concentrated by a constant discharge of steam, for the purpose as described.

6. The process of bleaching consisting in immersing at first the material in a solution 90 containing hydrofluoric acid, and in steaming the same, and in washing said material in a bath containing an alkaline earth compound, and again steaming said material, and in treating the same thereafter with boiling caustic 95 alkaline lye, which is kept concentrated by a constant discharge of steam, for the purpose as described.

In testimony whereof we have signed this specification in the presence of the subscribing witnesses.

HEINRICH THIES.
EMIL HERZIG.

Witnesses as to the signature of Heinrich Thies:

CHS. KRUEGER,
RUDOLPH FRICKE.

Witnesses as to the signature of Emil Herzig:

BENDERS CIÉ,
OTTO LUZ.